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## Ammonium Perchlorate Biodegradation for Industrial Wastewater Treatment

June 2000



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## LIST OF ACRONYMS

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AFB	Air Force Base
AFRL	Air Force Research Laboratory
AP	Ammonium Perchlorate
BOD	Biological Oxygen Demand
CBP	Carbohydrate Byproduct
COD	Chemical Oxygen Demand
CRDA	Cooperative Research and Development Agreement
CSTR	Continuous Stirred Tank Reactor
Cv	Control Valve Sizing Coefficient
FBR	Fluidized Bed Reactor
FRP	Fiber Reinforced Plastic
gpm	Gallons per Minute
HAP-1	Shorthand name for the perchlorate-reducing bacterium before its identification
HDPE	High-Density Cross-linked Polyethylene
HMX	Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
IPA	Isopropyl Alcohol
ISE	Ion-Selective Electrode
IWTP	Industrial Wastewater Treatment Plant
KCl	Potassium Chloride
KP	Potassium Perchlorate
NPDES	National Pollutant Discharge Elimination System
OB/OD	Open Burning/Open Detonation
O&M	Operations and Maintenance
PLC	Programmable Logic Controller
ppb	Parts per Billion
ppm	Parts per Million
RCRA	Resource Recovery and Conservation Act
RFD	Reference Dose Value
RT	Residence Time
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids

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Several individuals and organizations participated in this demonstration and provided review, guidance, and information that were valuable to the success of this project. Details of points of contact are provided in Appendix A.

- Air Force Research Laboratory
- Applied Research Associates, Inc.
- Thiokol Corporation

*Technical material contained in this report has been approved for public release.*

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## 1.0 EXECUTIVE SUMMARY

Ammonium perchlorate (AP) is the oxidizer and primary ingredient in solid propellant for most large rocket motors. High-pressure water washout is the currently accepted process of AP removal for component and ingredient recovery in remanufacture or demilitarization programs. In addition to manufacturing and testing activities, the AP recovery process generates significant quantities of wastewaters that contain various concentrations of perchlorate, salts, corrosion inhibitors, metals, and other propellant ingredients. These waste streams must be treated as a hazardous waste at a cost in excess of \$1.00 per gallon. The Minuteman III propulsion remanufacture program will remove over 35 million pounds of propellant from 1200 first and second stage motors in order to recover and reuse the cases.

Increased regulatory constraints have curtailed the ability of the Air Force to dispose of rocket propellant by open-burning, open-detonation (OB/OD), or static firing. All of the major DoD propulsion contractors currently have either an AP disposal problem or a groundwater contamination problem that could delay, add unnecessary costs to, or otherwise jeopardize major production programs.

In the early 1990s, the Air Force Research Laboratory (AFRL) developed an anaerobic biodegradation process to treat aqueous perchlorate waste streams. Following successful laboratory work, this Environmental Security Technology Certification Program (ESTCP) project demonstrated the operation of a prototype biodegradation system in 1997, first at Tyndall Air Force Base (AFB), and later at the Thiokol Corporation (Cordent Technologies) production facility near Brigham City, Utah. The biodegradation process provides a safe, low-cost, environmentally acceptable method for disposal of AP process wastewater and secondary waste brine streams associated with production, remanufacturing, testing, and demilitarization.

The perchlorate biodegradation prototype has been in continual operation at Thiokol since inoculation and startup on December 8, 1997. To reduce operating costs, several low-cost, carbohydrate-based wastes were evaluated for use as nutrients. First, successful operation was demonstrated using a brewer's yeast and cheese whey mixture as nutrient sources. Carbohydrate byproduct (CBP) was then used as a lower-cost nutrient to further reduce costs. CBP is a low-cost, pumpable byproduct from the food processing industry that contains amino acids, proteins, sugars, and micronutrients, which aid system performance. CBP demonstrated better performance than other nutrients and performed well over a broader concentration range.

During 1999, the prototype biodegradation treatment plant at Thiokol destroyed 15,400 pounds of perchlorate. Conversion from the yeast-whey nutrient blend to CBP took place in May 1999. Concentrated perchlorate brine ranging from 2,800 to 41,000 parts-per-million (ppm) was diluted 5-20% to provide a weighted-monthly average feed concentration between 300 and 4,600 ppm to the anaerobic system. Good performance at 10-20 hours residence time has been maintained since conversion. Perchlorate in the treated effluent, which was discharged to the sewer, was reduced to 4-400 parts-per-billion (ppb). Actual nutrient and chemical costs were reduced more than 90%, from an average of \$1.76 to \$0.16 per pound of perchlorate reduced. The treated effluent was no longer hazardous due to the destruction of the perchlorate, the primary regulated contaminant, although the residual Chemical Oxygen Demand (COD) and the Total Suspended Solids (TSS) levels in the treated effluent were each as high as 2,000 ppm. Direct sewer discharge would likely be allowed by

receiving sewage treatment facilities if the process were implemented elsewhere, but an additional treatment surcharge may be assessed.

The co-processing of three alternative effluents with perchlorate wastewater was also investigated at the laboratory scale to see whether their organic constituents had an inhibitory effect on perchlorate reduction and whether there was any contribution to system nutrient requirements. Isopropyl alcohol (IPA) contaminated with the explosive HMX exhibited some inhibition at concentrations above 1%. Ethylene glycol enhanced performance and could be used as a sole carbon source. Brulin solution (an aqueous degreaser) had little effect on performance. Laboratory studies were also performed on potential co-contaminants boron, aluminum hydroxide and cadmium. Some inhibition of perchlorate reduction occurred at higher concentrations of cadmium and boron. These contaminants could impact performance by bio-accumulating in recycled biomass. Aluminum hydroxide ion did not affect performance.

The budgetary capital cost estimate for a full-scale plant to treat up to 4 gpm of diluted perchlorate brine at the productivity of the Thiokol prototype was \$225 million. Estimated treatment costs were approximately \$0.35 to \$1.40 per gallon of undiluted brine, including a surcharge of \$0.05 per gallon undiluted brine for residual COD and TSS treatment. On a normalized basis, the estimated treatment cost was \$3.10 per pound of perchlorate.

Incorporation of this prototype into Thiokol's perchlorate recovery and wastewater treatment processes has optimized operations and reduced operating costs. However, the Thiokol prototype process is thought to be currently operating at only 25-40% of potential capacity. New programs associated with Minuteman III remanufacture and the Space Shuttle will result in even greater demands on the performance of the biodegradation prototype at Thiokol.

Several operational changes and modifications were recommended to improve performance by enabling a reduction of residence time, reducing temperature, operating the reactors in series, eliminating the clarifier and biomass recycle, and directly feeding undiluted nutrients and supplements. Minor hardware and software modifications would also be necessary. Operating at improved reactor productivity as a result of these modifications would reduce the estimated cost of perchlorate treatment to as low as \$0.15 per gallon of undiluted brine, or \$0.85 per pound of perchlorate destroyed. At this improved level of performance, cost savings compared to conventional processing methods, would yield a simple payback of 2.5 - 6.5 years on the capital investment required to implement the biodegradation system.

## 2.0 TECHNOLOGY DESCRIPTIONS

### 2.1 BACKGROUND DEVELOPMENT

Biodegradation was recognized by the Air Force Research Laboratory (AFRL) in 1989 as a potential process for treating dilute ammonium perchlorate (AP) waste streams and for remediating contaminated soil and groundwater. Attaway and Smith<sup>1</sup> isolated an organism designated HAP-1 capable of reducing perchlorate. Laboratory studies were conducted on aqueous AP solutions, in batch mode and in continuously stirred tank reactors (CSTRs).

The technology is a low-cost, complete destruction, anaerobic biodegradation process for industrial wastewaters. It utilizes the perchlorate ion ( $\text{ClO}_4^-$ ) in process wastewater as a terminal electron acceptor to convert it to chloride ( $\text{Cl}^-$ ). The process requires supplementation with nutrients to provide a source of both carbon and other essential micronutrients for the HAP-1 organism. The process is able either to directly treat ammonium perchlorate (AP) wastewaters or to treat potassium perchlorate (KP) brine waste streams generated by AP recovery processes. Perchlorate can be reduced from a concentration greater than 1.0% to a concentration below detection limits ( $< 0.5$  ppm).

Process variables that affect perchlorate reduction performance include temperature, pH, nutrient type, nutrient concentration, residence time, and perchlorate ion concentration. Nutrients must be commercially available, relatively low cost, and demonstrate good performance with respect to perchlorate reduction. The most promising nutrients identified in bench-scale studies were dried brewer's yeast and yeast extracts. Typical treatment conditions were:

Temperature	37-42 °C
pH	6.5-7.6
Residence Time	8-24 hours
Perchlorate Concentration	$< 6000$ ppm
Degradation Rates	125 mg/l per hr

Most perchlorate effluents contain numerous additional contaminants. The process can be adapted to almost any perchlorate problem, each of which has its own unique set of contaminants and contaminant concentrations that must be accommodated. Reduction of the perchlorate anion ( $\text{ClO}_4^-$ ), which is the primary regulated contaminant in AP and KP effluents, is not inhibited by the presence of different cations ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ). Other contaminant anions including nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and chlorate ( $\text{ClO}_3^-$ ) are also reduced. This is important since they represent degradation products or components of other energetic materials and corrosion inhibitors that may be present with perchlorate. The other products of reduction, organic acids, chloride and nitrogen, are discharged. Effluents from this process can be discharged directly to conventional sewage treatment facilities.

Laboratory efforts culminated in the positive identification of the bacterium in the mixed culture responsible for perchlorate reduction as *Wolinella succinogenes*.<sup>2</sup> When strict anaerobic conditions were maintained, very stable, predictable perchlorate reduction was obtained at rates exceeding 0.5 g/l per hour. In addition, it was successfully demonstrated that the HAP-1 mixed culture could destroy AP in the presence of other energetic compounds including nitroglycerin, nitramines,

stabilizers, and plasticizers. One patent has been granted on this process<sup>3</sup> and additional patents are pending.

Process optimization efforts focused on reducing operating costs, tailoring process variables, and reconfiguring operations to treat representative industrial wastes. These efforts resulted in an increased robustness of the process to effectively treat effluents containing over 1.0 percent (10,000 ppm) perchlorate. Perchlorate can also be reduced in effluents with a high salt content ( $> 2.3\%$   $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ) and other impurities ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ), and over a broad temperature range (20-42 °C). Low-cost nutrients were used successfully to lower the primary operating expense. Dried brewer's yeast could be used directly, without extracting the critical nutrients. Although this increased Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) concentrations in the effluent, the total nutrient requirement and costs were reduced. Studies showed that dried, sweet cheese whey might also be an effective nutrient by itself or in mixtures with brewer's yeast. Cheese whey is more soluble than brewer's yeast and only one fourth the cost.

Pilot-scale work was conducted at Tyndall AFB in 1995 using actual effluent from Minuteman Stage 2 propellant washout supplied by Aerojet Corporation's Propulsion Division. Bench-scale treatability studies were performed in 1996 on both ammonium perchlorate and brine waste streams from Thiokol's perchlorate recovery and ion exchange processes using brewer's yeast and cheese whey as nutrient sources, reduced temperatures, and flexible operation of two reactors in either parallel or series. These studies provided the necessary information for adapting an existing pilot scale system to meet Thiokol's needs.

## 2.2 PRODUCTION-SCALE PROTOTYPE DESIGN

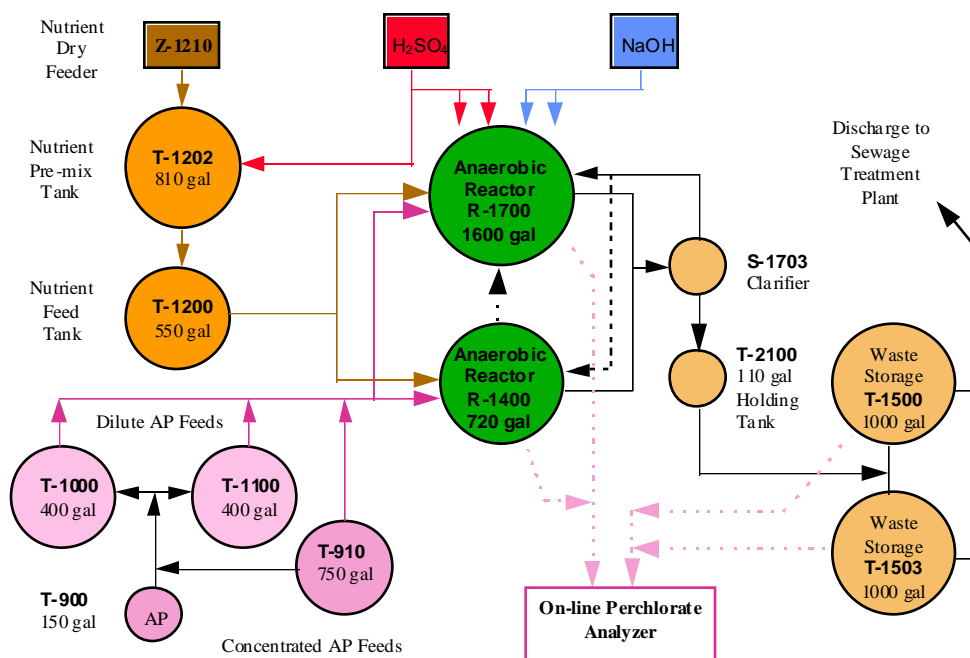
A schematic of the prototype is provided in Figure 1. The general requirements for developing production-scale demonstration system design were:

- Robust process design to provide stable, dependable, repeatable operation
- Flexibility to treat a broad range of feed rates and perchlorate and brine concentrations
- Ability to use low-cost nutrients for low-cost operation
- Maximum automation and flexibility of process control

Specific design requirements included:

- Capacity to treat 450 gallons per day of saturated perchlorate brine
- Treat up to 1.0% perchlorate in diluted feed
- Reduce perchlorate to  $< 0.5$  ppm in a single stage
- Two anaerobic reactors that could be operated in parallel or series
- Prepare and feed low-cost, high-solids, nutrient slurry
- Materials of construction to be able to handle corrosive environment of perchlorate, sulfuric acid, and sodium hydroxide
- Process variable control using Programmable Logic Control (PLC):
  - ✓ Temperature - control both reactors in the 20-40 °C range
  - ✓ pH - control reactors near pH 7.1 and nutrient slurry in the 2.0-4.0 pH range
  - ✓ Residence times - nominal 18-24 hours on diluted feed, capable of 12-30 hours
  - ✓ Reactor inerting - sparge with nitrogen generated by a membrane system
- Process control - on-line perchlorate analysis providing feedback for flow control

## Identification and Arrangement of Process Equipment



**Figure 1. Ammonium Perchlorate Biodegradation Process Layout.**

Effluent from the anaerobic reduction has an elevated COD/BOD content directly proportional to the amount of nutrient added to the reactor. Local sewage treatment facilities may accept these new high COD/BOD effluents at a surcharge. If not, aerobic post-treatment would be required to lower the organic content.

### 2.3 ALTERNATIVE NUTRIENTS

Laboratory studies identified specific micronutrients necessary for the reduction of high concentrations of perchlorate. The discovery of the benefits of micronutrient addition led to further evaluation of macronutrients (carbon sources) for perchlorate biodegradation. Perchlorate was successfully reduced using many alternative nutrients. These included cheese whey, marshmallow waste, fruit juice wastes, sugars, starches, and acetate. The marshmallow waste was evaluated because it is very abundant and very inexpensive (\$10/ton). The marshmallow waste worked very well at concentrations equivalent to brewer's yeast, but had drawbacks. Another inexpensive (\$25/ton) food processing waste, carbohydrate byproduct (CBP), was evaluated for use in this process. It showed more promise without the drawbacks of the marshmallow waste.

## **2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY**

### **2.4.1 Advantages**

The perchlorate biodegradation process:

- Operates at near ambient conditions - inexpensive equipment & operation
- Is fast for an anaerobic biodegradation process - reduces the size and cost of equipment
- Accepts high concentration perchlorate feed ( $> 1.0\%$ ) to the CSTR and reduces perchlorate to  $< 0.5$  ppm in a single stage
- Can reduce perchlorate in the presence of  $>2\%$  salts and other inorganic contaminants
- Is less expensive than concentration/recovery processes for low concentrations of perchlorate
- Reduces the generation of hazardous wastes
- Minimizes adverse impact of environmental compliance to DoD support operations
- Reduces the cost of solid rocket propellant and large rocket motor disposal
- Reduces the cost of weapon system production - specifically the Minuteman III Propulsion Remanufacture Program
- Facilitates component, propellant, and propellant ingredient recovery and reuse
- Enables the continued use of AP, a critical defense material, in propulsion systems

### **2.4.2 Limitations**

- There is an upper limit to steady-state, equilibrium perchlorate concentrations in a reactor — concentrations above 6000-10,000 ppm appear to inhibit perchlorate reduction
- At perchlorate concentrations above 4000 ppm, processing costs increase linearly with perchlorate concentration due to a proportional nutrient requirement
- BOD/COD values for the treated effluent are proportional to nutrient addition, and much higher than for settled domestic sewage.

This process is inherently reliable because of its near ambient operating conditions. However, loss of temperature or pH control could destroy microbes in the reactor and force re-inoculation of the system. This could interrupt operations for several days. The process design shown in Figure 1, with dual anaerobic reactors, a clarifier, effluent storage tanks, and on-line perchlorate analysis providing feedback control, significantly mitigates against potential loss of biological activity. If perchlorate concentration begins to rise in a reactor indicating loss of perchlorate reduction activity, the control system limits the perchlorate effluent feed, helping to preserve viable microbes in all process vessels. If necessary, a reactor can quickly be re-inoculated by recycling effluent from the second reactor, clarifier, or effluent storage tanks.

## **2.5 REGULATORY ISSUES**

Alternative processes for disposal of propellants are required to achieve compliance with the following: Clean Air Act Amendments (CAAA) 1990, the Federal Water Pollution Prevention and Control Act (FWPPCA) 1987, the Resource Conservation Recovery Act (RCRA), and the Federal Facility Compliance Act 1992 (P.L. 102-386).

The US Environmental Protection Agency (EPA) has issued a provisional Reference Dose Value (RFD) that could restrict discharge of AP to less than 1 ppm and severely impact DoD propulsion contractors. In 1992 the EPA identified a no observable adverse effects level (NOAEL) of 0.14 mg/kg/day for the health effects of perchlorate on release of iodine from the thyroid and inhibition of iodine uptake. When standard dose criteria and an uncertainty factor of 1000 were applied, a 4 parts-per-billion (ppb) drinking water criterion was obtained. In 1995, the EPA reduced this uncertainty factor to 300, which made perchlorate concentration limits in drinking water range from 4-18 ppb. In 1997, improved analytical methods enabled perchlorate detection limits to decrease from approximately 1 ppm to 4 ppb.

In February 1997, the California Department of Health Services (DHS) began to analyze certain drinking water wells in Sacramento County and southern California suspected of containing perchlorate. As contaminated wells began to be identified, the California DHS reviewed the EPA data and established an 18 ppb action level for perchlorate in drinking water. On August 1, 1997, DHS informed drinking water utilities of its intention to develop a regulation that includes perchlorate as an unregulated chemical for which monitoring is required.

## **2.6 CONVENTIONAL PROCESSING OF AMMONIUM PERCHLORATE WASTE STREAMS**

There are at least eight rocket motor production facilities, two perchlorate-manufacturing facilities, and many ordnance production facilities in the United States. Before current Resource Conservation and Recovery Act (RCRA) and other environmental laws were enacted and enforced, propellant, and propellant ingredient wastes were disposed of by open burning and open detonation (OB/OD). OB/OD is now severely restricted. Aqueous effluents were also collected in evaporation ponds, or, in some cases, discharged to the environment.

Conventional technologies presently in use remove, but do not destroy, the perchlorate. In the industrial wastewater treatment plant (IWTP) at its production facility near Brigham City, UT, Thiokol treats concentrated AP effluents by evaporation and ion exchange to replace ammonia by sodium, followed by ammonia stripping. Excess potassium chloride (KCl) is then added to effect the precipitation of potassium perchlorate (KP). This results in a 10-30% salt ( $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ ) brine solution containing 3,000-40,000 ppm perchlorate and additional nitrate and nitrite.

## **2.7 COMPETING ALTERNATIVE TECHNOLOGIES**

There is no other perchlorate destruction technology (other than OB/OD) at this level of maturity. The most promising competitive destruction technologies are catalytic and electrochemical processes. While both have been demonstrated to work in the laboratory to some degree, there are many technical hurdles to overcome before they can be seriously considered for full-scale implementation. Although biodegradation of perchlorate requires nutrient, catalytic processes require effluent pretreatment, electricity, expensive precious metal catalysts, and additional reactants such as reducing agents (hydrogen gas). The major concerns are catalyst fouling, long-term performance, destruction efficiency and cost.

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## 3.0 DEMONSTRATION DESIGN

### 3.1 PERFORMANCE OBJECTIVES

This demonstration provided a production-scale, operational validation of the ammonium perchlorate (AP) anaerobic biodegradation process that was developed by the Air Force Research Laboratory. The primary objective of this effort was to reduce nutrient consumption and cost. The performance goal was to optimize nutrient concentration to achieve perchlorate reduction rates equal to or greater than 0.5 grams/liter/hour. The treatment objective was to reduce all the perchlorate in a contaminated brine effluent to the lower detection limit for state-of-the-art perchlorate analytical methods for process wastewater, which is 0.5 ppm. However, the demonstration was to be considered successful if the treated effluent concentration was kept below Thiokol's permit limit of 10 ppm. Another objective was to demonstrate on-line perchlorate analysis for process control. By adjusting process control logic, residence time and nutrient consumption could be minimized and the process optimized towards cost and/or capacity.

A combination of laboratory studies and operational changes to the prototype was employed to test alternative nutrient performance. In addition, the effect of other site wastewater and co-contaminants were evaluated. Specific sub-objectives for this effort included:

**Replace brewer's yeast and cheese whey with alternate nutrient source.** Brewer's yeast (\$0.50-1.00 per lb) and cheese whey (approximately \$0.20 per lb) are expensive nutrients, which could be substituted without affecting perchlorate reduction performance.

**Simultaneously process other effluents.** Other effluent streams studied were spent ethylene glycol coolant, isopropyl alcohol (IPA) contaminated with HMX, and Brulin solution (an aqueous degreaser).

**Evaluate the effect of co-contaminants.** Co-contaminants of interest include aluminum, cadmium, and boron. Hydrolysis of aluminized propellants results in the potential for high concentrations of  $\text{Al}(\text{OH})_4^-$  in solution. Cadmium has been observed in wastewater from certain propellant removal operations. Boron originates either from boron containing igniter components or corrosion inhibitors used during propellant removal and recovery operations.

### 3.2 DEMONSTRATION SITE/FACILITY BACKGROUND AND CHARACTERISTICS

#### 3.2.1 Tyndall AFB Demonstration Site

The first phase of the demonstration occurred at Tyndall AFB, Florida. The existing facility that housed the 1995 and 1996 demonstrations of the original pilot-scale system were used. Use of the existing infrastructure, laboratory facilities, and experienced operators minimized risks during system trouble-shooting and checkout.

#### 3.2.2 Thiokol Demonstration Site

Thiokol's Utah operations are located near Promontory, 25 miles northwest of Brigham City. Thiokol has been involved in propellant removal, component recovery, demilitarization, and large

rocket motor production for over 35 years. In addition to production programs for tactical systems such as the Standard Missile, stages or components of major Navy and Air Force Strategic systems have been produced at this facility. These include Minuteman I, II, and III, Peacekeeper, and Trident I and II. Space Shuttle Solid Rocket Motors (SRMs) are also manufactured at this facility.

In the early 1990s, Thiokol Corporation, constructed an industrial wastewater treatment plant (IWTP) at its Brigham City production facility, and deactivated its evaporation ponds. Aqueous treatment costs at Thiokol were in excess of \$1.00 per gallon and these treatment processes generated sludges, spent activated carbon sorbents, spent ion exchange resins, salts, and brine solutions containing AP. The original National Pollutant Discharge Elimination System (NPDES) permit at the Thiokol IWTP for perchlorate discharge required treatment to an upper limit of 10 ppm. Thiokol implemented the perchlorate recovery and ion exchange processes to achieve this requirement. However, these processes were creating high levels of total dissolved solids (TDS), which would likely violate the NPDES permit requirement of 3800 ppm during any major remanufacture program, such as the Minuteman III, or a disposal effort such as the Titan solid rocket motor (SRM) disposal program. The prototype perchlorate biodegradation process was integrated into this existing waste treatment facility.

Thiokol was selected for the following reasons:

- Perchlorate wastes are generated from production and demilitarization operations
- Perchlorate wastewater is segregated from wastewater containing other energetics
- A potassium perchlorate recovery process is in operation that produces a perchlorate containing brine effluent
- A second AP recovery process has recently begun operation. It may also produce an AP effluent that requires potassium precipitation and/or perchlorate biodegradation
- A new, state-of-the-art, industrial wastewater treatment plant is operational
- A new sewage treatment facility has been constructed and is in operation. It can easily treat high BOD/COD effluents generated by the AP biodegradation process.

### **3.3 SITE/FACILITY DESCRIPTIONS**

The Tyndall AFB site required minimal preparation for this demonstration. The most significant modification was converting the facility to 480 VAC, 3-phase service.

At the Thiokol site, the entire prototype system was housed in a new building to protect it from the elements and low temperatures, located adjacent to the existing IWTP (Building M-705). Thiokol provided infrastructure and connection to all utilities, effluent streams, and the sewage treatment facility. Typical effluent from the ion exchange and potassium precipitation units were very high in TDS (150-300 g/l) and relatively low in perchlorate (5000 ppm). Although effluents were delivered to the process in batches and stored before treatment, the process itself was operated continuously, 24 hours per day, seven days per week.

### **3.4 PHYSICAL SET-UP AND OPERATION**

The demonstration occurred in two phases after modification of the original pilot scale system. The transportable, prototype production-scale system was first assembled at the existing test site at

Tyndall AFB to conduct functional and process demonstrations. Process control and performance were demonstrated with two bioreactors in both parallel and series operational configurations. Wastewater shipped from Thiokol was diluted prior to being fed to the reactors, which resulting in a feed of 2% KCl brine contaminated by perchlorate. The system was operated at residence times of 18-24 hours at temperatures of 35-40 °C for 8 weeks in summer 1997. Upon successful completion of the Tyndall AFB demonstration, the system was modified, disassembled, transported to Thiokol, and reassembled. The validation testing at Thiokol demonstrated technical and cost performance of the prototype biodegradation process integrated into the existing industrial waste treatment facility. It was inoculated in December 1997. Through a Cooperative Research and Development Agreement (CRDA), performance and cost data were collected for two years after the end of the ESTCP funding support. Complete details of the physical set-up and operation of the prototype may be found in the ESTCP final report<sup>4</sup>.

### **3.4.1 Inoculation and Startup**

An important step in startup was inoculating the reactor with the HAP-1 microbe consortium. Lyophilized (freeze-dried) microbial samples (obtained from active laboratory reactors at Tyndall AFB) were used to facilitate startup of field systems (or to recover from a process upset). Lyophilized samples were added directly to a growth medium containing nutrient (5-25 g/l of brewer's yeast, yeast extract and/or sweet cheese whey), pH buffers, and perchlorate (500-1000 ppm). The culture was grown up at temperatures of 25 to 40 °C in an anaerobic chamber or in sealed 100 mls bottles, in which perchlorate concentration was monitored and pH adjusted daily to maintain pH 7.0-7.5. Transfers, first to 1 liter bottles and then to 20 liter carboys were necessary before inoculating the reactor. In the reactor, 200 gallons of 12 g/l brewer's yeast containing 1000 ppm perchlorate were brought to pH 7.0 and a temperature of 30-40 °C, and subsequently sparged with 2.0 ft<sup>3</sup>/min of nitrogen. The reactor was inoculated by adding four 20-liter carboys to 200 gallons of media. When perchlorate concentration began to drop rapidly, additional nutrient, buffers and perchlorate effluent were metered into the reactor continuously at flow rates proportional to a 24-hour residence time until the reactor was at capacity.

### **3.4.2 Process Operation**

Typically, a CSTR process requires less than five or six residence times to stabilize after a condition change (i.e., five or six days when operated at a 24 hour residence time). However, in a biological process, condition changes occasionally produce a lag-time while the organisms adapt to the new environment. Therefore, for some conditions, it was desirable to operate for extended periods of time to ensure the culture had fully adapted (either positively or negatively) to the new condition. The effluents from the anaerobic reactors were discharged directly to the existing sewage treatment facilities.

### **3.4.3 Laboratory Screening Tests**

#### **Alternative Nutrients**

Laboratory tests were conducted to screen the performance of alternative nutrients to determine the effect of nutrients and nutrient concentrations on perchlorate reduction performance. The most rapid and useful screening tool employed was a small (100-1000-ml) bottle inoculation test, in which 160 ppm perchlorate, 0.4-6.7 gm/l CBP nutrient, and phosphate buffers were added, the pH adjusted to

7.5-8.0, and a 5-10% inoculum from an active culture added. Bottles were sealed, then transferred to an anaerobic chamber and incubated at 35 °C. Although bottle tests did not directly correlate to CSTR performance, they indicated factors that may affect perchlorate biodegradation rates.

### **Co-Processing of Effluents**

Thiokol provided three effluents that could potentially be co-processed with perchlorate wastewater. These potentially biodegradable, organic-based effluents were ethylene glycol, isopropyl alcohol (IPA), and Brulin solution. The objectives for the laboratory screening study were to: (1) determine whether perchlorate reduction was inhibited, and (2) determine whether these materials could contribute to nutrient requirements for perchlorate reduction. To best simulate the co-processing of the other effluents, bottle tests were prepared with 2% KCl solution, 400 ppm perchlorate, and 0-1.7 g/l CBP. The bottles were then inoculated with 5 ml of brewer's yeast inoculum and incubated in an anaerobic chamber.

### **Co-Contaminants**

The potential inhibitory effect of likely co-contaminants boron, cadmium and aluminum hydroxide was investigated using 0.9-1.7 g/l CBP.

Further details of procedures employed are available in the performance optimization report 5.

## **3.5 MONITORING/SAMPLING PROCEDURES**

Technicians and operators were trained in proper sampling procedures and Quality Assurance/Quality Control (QA/QC) protocols used by AFRL at Tyndall AFB. Samples were taken from various sample ports on the prototype facility. All valves and hoses used for sample collection were flushed prior to sample collection to ensure fresh samples. There were two types of sample media: 1) aqueous feed solutions consisting of perchlorate anions, various salts, corrosion inhibitors, and other inorganic components, and 2) biosludge from the reactors. The sampling procedure and corresponding analyses were the same for both types of sample media.

Field duplicates were collected and analyzed for the same parameters as the associated samples. They were preserved, transported, and documented in the same manner as the samples. Frequency of field duplicate sampling was a minimum of one or 10% of the total number of samples taken. Split samples were also taken, preserved, transported, and documented using the same protocols as the related samples. Aqueous or dilute biosludge samples were split due to the large variability in solids content. The samples were mixed in a large, appropriately cleaned, sample containers and aliquots were poured into the appropriate labeled sample containers. Split sampling was conducted once per sample batch. Samples were taken daily and placed in polypropylene bottles to be frozen immediately, except for samples required for pH testing, plate counts, and solids tests which were performed upon receipt. Samples taken for plate count determinations were kept as anaerobic as possible, and the plating procedure was executed within 30 minutes of sample collection.

## 3.6 ANALYTICAL PROCEDURES

### 3.6.1 Types of Analyses

Sampling and data collection consisted of monitoring the process variables and analyzing the influent and effluent streams. Analyses consisted of:

- 1) Anions -  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{2-}$ , & others if suspected
- 2) Cations -  $\text{NH}_4^+$
- 3) Chemical oxygen demand (COD)
- 4) Total suspended solids (TSS) and total dissolved solids (TDS)
- 5) HAP-1 and other microbe cell counts
- 6) Total Organic Carbon (TOC)

Metals present in low concentrations were not thought to present a problem to the process, and were not routinely analyzed.

### 3.6.2 Selection of Analytical Methods

The primary method employed to determine the concentration of the perchlorate anion was to use an ion ( $\text{ClO}_4^-$ ) specific electrode (ISE), which can accurately detect perchlorate concentrations in reactor effluents to a lower limit of 10 ppm. The prototype unit was equipped with an online perchlorate analyzer, which was a dual channel unit designed to be used in both automatic and manual modes, so this method was used to determine perchlorate concentration in both discrete and continuous samples.

The system PLC was configured to automatically trigger the sample loop pumps and, after a time delay, trigger the analyzer to sample the reactors and storage tanks in pairs, i.e., R-1400 and T-1500, then R-1700 and T-1503. During parallel operation, analyzer readings were accurate (within 10%) for the brine even in the presence of large concentrations of chloride. During series operation, the readings were only reliable for the second reactor (R-1700) and the storage tanks. The perchlorate concentrations of the first reactor were outside the low concentration range. There is an upgrade available for the existing system that would enable the unit to perform sample dilutions and provide analysis at any concentration.

Perchlorate-containing effluents have high TDS concentrations and several anions known to interfere with perchlorate ISEs. Interfering anions such as chloride and nitrite cause measurements to vary over 10% at perchlorate concentrations between 1 and 100 ppm. In addition, low ppm measurements are at the limit of capability for the ISE methods. Therefore, although the ISE is a standard method for perchlorate anion concentration, an ion chromatography (IC) method, which can accurately detect perchlorate levels down to 0.5 ppm, was also employed to determine lower perchlorate concentration levels. This method was developed in 1992 using a Dionex DX-300 series IC instrument employing a C-18 High Performance Liquid Chromatography (HPLC) reverse-phase column and conductivity detection.

All other anion determinations ( $\text{ClO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{2-}$ ) except nitrite ( $\text{NO}_2^-$ ) were completed with the Dionex DX-300 series IC instrument employing an AS-11 Ion Pac column from

Dionex and conductivity detection. The Dionex system was computer controlled and integrated with AI-450 chromatography software. Nitrite analyses were conducted using Standard Method 4500-NO<sub>2</sub><sup>-</sup> A<sup>6</sup> using a CARY 3E-UV visible spectrophotometer.

COD was determined by the EPA-approved HACH method described in detail in the HACH Water Analysis Handbook<sup>7</sup>. The chloride ion can be a possible interference for this method. The COD catalyst powder contains mercuric sulfate to complex up to 1000 mg/l chloride. For higher chloride concentrations, the sample was diluted.

Total Organic Carbon (TOC) was determined using the Shimadzu TOC-5000 equipped with the ASI-5000 autosampler. This analytical method is also EPA approved.

## 4.0 PERFORMANCE ASSESSMENT

### 4.1 PERFORMANCE DATA: TYNDALL AFB DEMONSTRATION

#### 4.1.1 Startup

Both parallel and series operation were conducted successfully during the Tyndall AFB demonstration. The perchlorate used for inoculation and startup was prepared by diluting a concentrated AP solution obtained from a Minuteman Stage 2 propellant washout in order to conserve the brine solution supplied by Thiokol. The reactor was charged with approximately 200 gallons of dried brewer's yeast nutrient solution (10 g/l) and 1000 ppm of AP solution (made by diluting the AP concentrate 1:100). The temperature and pH were adjusted, and then the inoculum was added. The inoculum was grown from a lyophilized sample to validate the procedure presented in Section 3.4.1. Nitrogen was used to purge the reactor (R-1400) of oxygen to facilitate inoculation. When the perchlorate concentration began to drop, additional perchlorate and nutrient (5 g/l) solution were metered into the reactor. However, by the time R-1400 was full, perchlorate was completely reduced at a residence time of 24 hours. The effluent from R-1400 was fed to R-1700 along with AP and nutrient to inoculate the second reactor. With both reactors inoculated, parallel operation with AP feed was initiated. Table 1 describes the different feed materials used in the Tyndall AFB Demonstration.

**Table 1. Feed Effluent Characterization for Tyndall AFB Demonstration.**

	$\text{ClO}_4^-$ (mg/l)	$\text{Cl}^-$ (mg/l)	$\text{NO}_3^-$ (mg/l)	$\text{NO}_2^-$ (mg/l)	TDS (g/l)
$\text{NaClO}_4$ Brine	4,266	101,161	4662	299	271
AP Concentrate	123,000	2,286	346	128	125

While still in parallel mode, the feed was switched to a brine feed and mixed yeast/cheese whey nutrients supplementation. Dilution of the original brine concentration 1:10 (to approximately 500 ppm perchlorate) was necessary due to the unexpectedly high TDS level in the brine. Even this 10% solution resulted in a 2.71% salt content in the reactor before nutrient addition and pH adjustment. This was near the limit indicated by bench-scale studies for the onset of a significant deterioration in performance.

Nutrients from 50-lb bags were manually placed into the nutrient pre-mix tank (T-1202) where they were mixed with water and sulfuric acid into a concentrated slurry. Initially there was a concern that the flow control valves for the nutrient would easily plug from the yeast solids leading to nutrient deficiencies and possible perchlorate excursions in the reactor. Valve orifices had to be changed to larger Cv values than designed, and also a nutrient recirculation loop was installed from the control valves on R-1400 and R-1700 back to the nutrient feed tank (T-1200). Cheese whey is more water-soluble than brewer's yeast and, when combined with the dried yeast, reduced plugging in the feed lines and control valves.

Sulfuric acid was used mostly for setting the pH of the nutrient below 2.0 — a method of “sterilizing” the nutrient solutions to prevent fungal growth in the nutrient mix and feed vessels. It

was manually added due to recurring pump seal problems. Sulfuric acid consumption was minimal. The process by which the microbes destroy perchlorate is naturally acidic, and so caustic was mainly used to keep reactor conditions neutral.

A summary of the test conditions is provided in Table 2.

**Table 2. Test Condition Summary for Tyndall AFB Demonstration.**

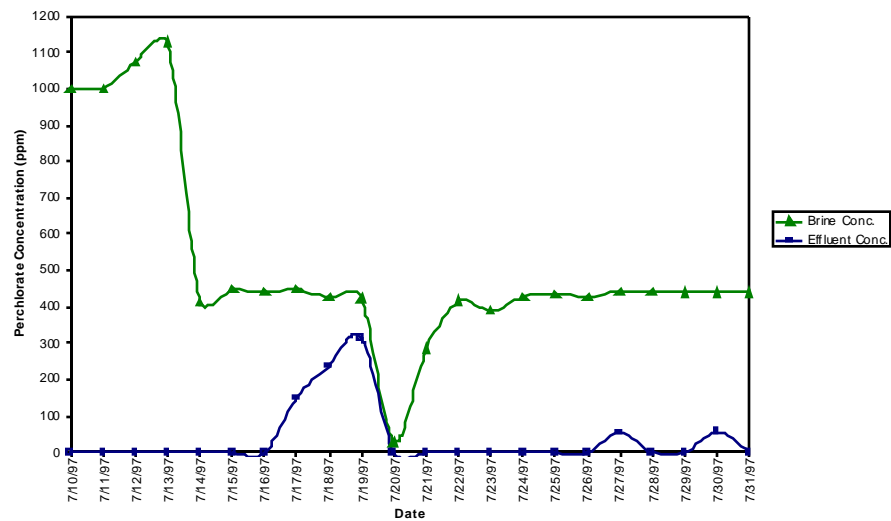
	Date Initiated	Reactor Config.	Effluent	Nutrient Feed		Res. Time	Other
			Feed Conc.	g/l	Type	hours	Events/Comments
1	7/1/97	Series	1000 ppm AP	5	100% yeast	24	Start-up
2	7/10/97	Parallel	1000 ppm AP	5	100% yeast	24	Start-up
3	7/14/97	Parallel	10% Brine	4	25:75 yeast: whey	24	Initiate brine feed Initiate whey nutrient
4	7/27/97	Parallel	10% Brine	4	50:50 yeast: whey	24	Increase yeast concentration
5	7/29/97	Parallel	10% Brine	4	100% yeast	24	Increase yeast concentration
6	8/1/97	Series	4000 ppm AP	16	100% yeast	24	Initiate series operation Initiate conc'd AP feed
7	8/7/97	Series	6000 ppm AP	24	100% yeast	24	Increase yeast concentration
8	8/30/97	Series	8000 pm AP	32	25:75 yeast: whey	24	Initiate whey nutrient

#### 4.1.2 Parallel Operation Using Brine Feed

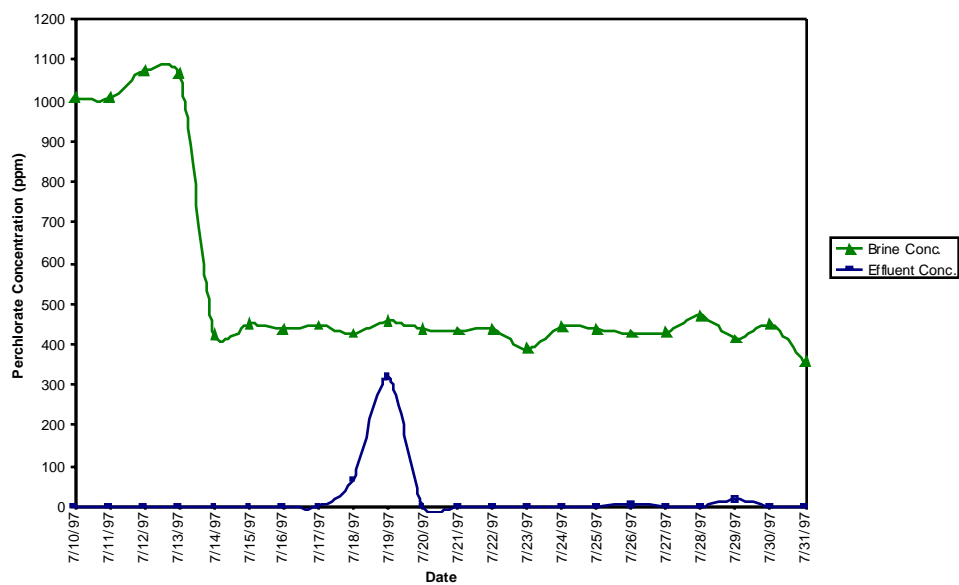
Overall, the system performed as designed. Figures 2 and 3 show brine and effluent concentrations for both R-1400 and R-1700 during parallel operations. The spike in perchlorate concentration in both reactors in Figures 2 and 3 was due to the microbial populations adjusting to high salt concentrations and a new nutrient source in the reactors. Figure 3 shows that the feed to R-1400 was temporarily interrupted for one day to aid in the adjustment. Both reactors recovered and performed well during the remainder of the parallel operation. Nutrient, brine and dilution flow rates were maintained very close to set point values (confirmed by totalizer readings) resulting in a nearly constant residence time. The operational data may be found in Tables 3 and 4 of Appendix B to the final report<sup>4</sup>. Anion data for both reactors may be found in Tables 8 and 9 of Appendix B of the final report<sup>4</sup>.

Temperature control for the Tyndall AFB demonstration was not optimal. The large glycol circulating pump in the loop caused significant heating of the process, and was switched off. However, reactor temperatures remained near the setpoint values.





**Figure 2. Parallel Operation at Tyndall AFB: Reactor R-1400 Brine and Effluent Concentrations.**



**Figure 3. Parallel Operation at Tyndall AFB: Reactor R-1700 Brine and Effluent Concentrations.**

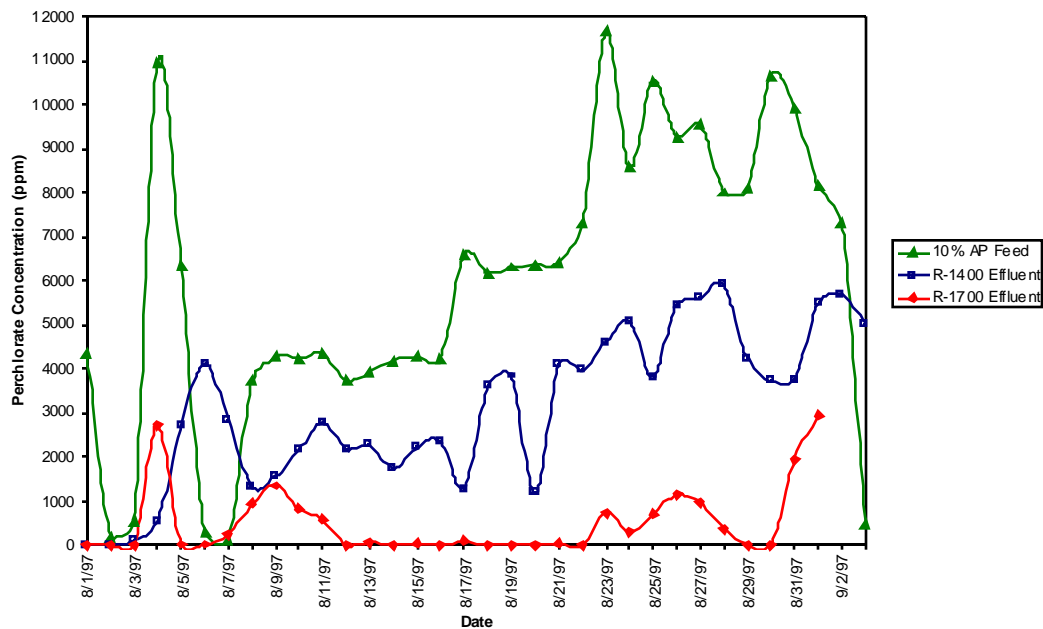
### 4.1.3 Series Operation Using Ammonium Perchlorate Washout Waste Feed

The objective of this portion of the Tyndall AFB demonstration was to show that concentrated (10-12%) perchlorate solutions could be treated anaerobically using a two-step process. Along with the necessary nutrient and set-point dilution water, concentrated AP washout solution was metered into the first reactor (R-1400) at a flow rate that would supply between 4000-6000 ppm perchlorate. Only a nutrient stream was fed to the second reactor (R-1700).

During series operation, the AP feed concentrations were progressively increased from 4000 ppm, to 6000 ppm, and then to 8000 ppm. The flow rate of dilution water was kept constant at a set point that determined nominal residence time. The AP flow rate was varied to give the desired dilution of the feed. Overall, the system performed in series as designed although nutrient plugging of the control valve with yeast solids was again a problem. However, Figure 4 shows that feed concentrations to R-1400 exceeded 10,000 ppm on several occasions. Following the switch to AP washout feed, residual KP in the feed lines precipitated out, causing plugging, flow control problems and periodic washing out of solid KP into the reactor. These large perchlorate spikes, coupled with high temperatures and elevated TSS levels, resulted in nutrient-limited conditions and caused perchlorate excursions from R-1700 after 8/22/97. However, with 4000 and 6000-ppm feeds, all the perchlorate was reduced in R-1700, indicating that 6000 ppm was a probable upper limit in feed concentration. Anion data for both reactors can be found in Tables 8 and 9 of Appendix B of the final report<sup>4</sup>.

Temperature ran high (100 - 115 °F) during series operation and could not be controlled. As the temperature increased in the reactors, perchlorate reduction became erratic. Above 42 °C (108 °F), perchlorate reduction was severely inhibited. High temperatures were partially attributed to the high solids content and long solids retention time in the reactors. Solids recycle was intended for recycling HAP-1 and unused nutrient. Operating the clarifier (S-1703) at 100% recycle resulted in a very long solids retention time and overwhelmed the reactors with suspended solids. TSS and COD in the clarifier overflow (i.e. treated effluent) rose to more than 6,000 and 12,000 ppm respectively. During series operation, no means of solids wasting was available. High recycle rates were acceptable for dilute feeds, but not for concentrated effluents, due to high nutrient feed rates. Therefore, the process was modified so that the recycle rate from the clarifier could be manually switched and controlled to either reactor, or to waste. (During parallel operations, recycling of solids did not present a problem because of low nutrient concentration.)

The operational data are provided in Tables 5 and 6 of Appendix B of the final report<sup>4</sup>.



**Figure 4. Series Operation at Tyndall AFB: Perchlorate Feed Concentration vs. Reactor R-1400 and Reactor R-1700 Concentrations.**

Several design modifications were identified as a result of the testing at Tyndall AFB:

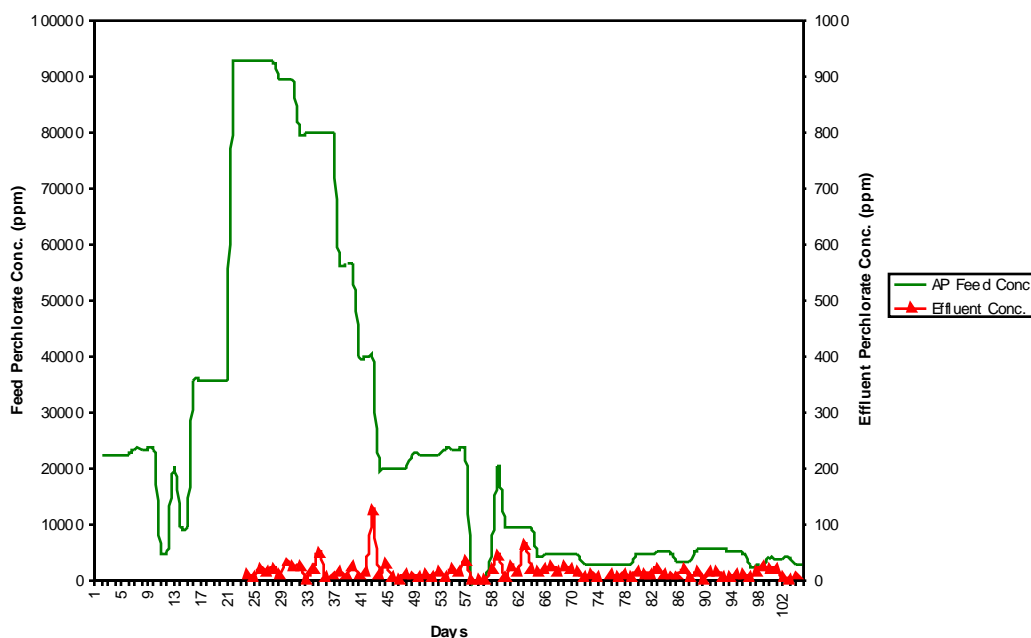
- Caustic and perchlorate pumps were modified from single-seal to double-seal heads
- A circulation loop was installed in the nutrient delivery system to minimize plugging problems
- Nutrient valve port sizes were increased
- Originally, samples for the online perchlorate analyzer were pulled from the underside of the vessels, but the lines and pumps plugged frequently. Samples were later taken from dip tubes inserted into the top of each sampled tank.
- Multiple two-way valves were configured on the clarifier recycle to permit control of solids recycle to both reactors and to waste independently
- A vent line was installed on the clarifier
- Start-up screens were developed to determine and change set points based on specific, operator input parameters
- Caustic was determined to be a more viable means of nutrient sterilization vs. acid

#### 4.2 PERFORMANCE DATA: THIOKOL VALIDATION

After startup, the system processed a total of 9,155 gallons of brine (received from the perchlorate recovery production facility at the IWTP) in 105 days operation, at a nominal residence time of 24 hours. The system operated exceptionally with no major upsets or perturbations requiring re-inoculation.. Because of the high TDS, the brine feed was diluted to 5-10% of its original concentration as it was fed to the reactors. Figure 5 shows that during the first two months of operation, the perchlorate concentration in the brine was variable and relatively high (20-90,000

mg/l) reflecting batch-to-batch variability as it was received. A different batch was fed to the reactors every 2-8 days. In addition, the effluent contained approximately 10,000 mg/l nitrite and 5000 mg/l nitrate.

Typical perchlorate concentrations in the reactor treated effluent were less than 20 ppm using the ISE probe method. These results almost always translated to near non-detect levels using IC. Nitrate levels were nearly completely reduced but little nitrite reduction was observed.



**Figure 5. Parallel Operation at Thiokol: Brine Feed and Treated Effluent Concentrations.**

Design modifications that resulted from the Thiokol validation were:

- Stainless steel (304) brine feed storage tanks T-1000 and T-1100 (400 gallons each) were both removed from service due to corrosion, which led to leaking. They were replaced with two fiber reinforced polyethylene (FRP) tanks, which were larger (775 gallons and 540 gallons) and provide more brine storage capacity.
- During installation, it was necessary to remove the strong perchlorate tank T-900 from the perchlorate feed skid. It was used as a feed tank for metering alternative nutrients and other contaminants into the reactors.
- Software modification and control improvements were also made to enhance system performance as necessary.
- Magnetic drive pumps replaced the double-seal head, centrifugal pumps for AP feed and pH control.

- Caustic was used for nutrient sterilization instead of acid.
- Citric acid replaced sulfuric acid for pH control-safer and more user-friendly.

### **4.3 LABORATORY STUDIES FOR IMPROVED PERFORMANCE**

#### **4.3.1 Evaluation of Alternative Nutrients**

Two nutrients were evaluated as alternatives to the brewer's yeast and cheese whey mixture used for Thiokol's prototype operation. First, a fruit juice waste, which could be obtained for transportation costs, was evaluated. It demonstrated acceptable performance but had some drawbacks such as low nutrient value (sugar concentration of approximately 4%) and instability (i.e., this material would ferment easily). The second alternative was a carbohydrate by-product (CBP) from a food processing operation. This liquid nutrient was concentrated in sugars, proteins, and minerals and, therefore, inherently stable providing the possibility of long term storage without fermentation or spoiling. Further details of procedures employed are available in the performance optimization report<sup>5</sup>.

Both nutrients effectively degraded perchlorate after a one to two day induction period. However, several significant differences in performance were observed. The fruit juice waste appeared to cause a longer induction period before perchlorate reduction was observed. Also, perchlorate was reduced at a slower rate with fruit juice than with CBP, and appeared to be negatively impacted by both high and low fruit juice concentrations. CBP performed better than fruit juice waste and also over a broader concentration range. Therefore the CBP nutrient would be more amenable fluctuating brine perchlorate concentrations, and better able to handle process upsets. The CBP was selected as the nutrient for testing in the Thiokol prototype process.

#### **4.3.2 Evaluation of Other Effluents**

##### **Ethylene Glycol**

The ethylene glycol solution provided by Thiokol was a concentrated effluent from heat exchanger equipment and from vehicle use. In a test with ethylene glycol and CBP nutrient, addition of glycol improved perchlorate reduction performance in comparison to the control not containing glycol. Perchlorate reduction was also accomplished using ethylene glycol alone as the primary nutrient. The actual reduction rate observed was less than rates with CBP, but complete perchlorate reduction was demonstrated. These results show that not only could ethylene glycol be used in this process to enhance performance of CBP-type nutrients, but that it could also be used as a carbon nutrient.

##### **Isopropyl Alcohol (IPA)**

Isopropyl alcohol and water solution is used to desensitize HMX during shipping. An approximately 50% IPA solution is recovered from HMX drying operations and typically contains low concentrations of HMX. The addition of the IPA did not improve performance over the control. Also, high IPA concentrations greater than 1% may have inhibited perchlorate reduction. While these results indicated that IPA should not be used as a primary nutrient source, it is possible that acceptable performance might be obtained after additional acclimation of the microbial culture to the IPA. "As received" IPA solution could be co-processed at approximately 1% concentration without inhibiting perchlorate reduction performance. The fate of the HMX present was not determined. However, other studies have shown that the culture used in this process will completely

remove the nitro- functionality of explosive compounds (aromatic and non-aromatic). Therefore, it is likely that the HMX present was completely destroyed.

### **Brulin Degreaser Solution**

An aqueous degreaser solution (trade name Brulin) is another effluent produced on site at Thiokol. Spent Brulin solution may contain organics and other contaminants, but a detailed analysis was not conducted. Addition of Brulin and CBP nutrient did not appear to improve perchlorate degradation performance over the control. While the results indicated that Brulin should not be used as a primary nutrient source, it is possible that acceptable performance could be obtained after additional acclimation of the microbial culture to the Brulin. The results indicated that Brulin may be co-processed at concentrations up to 10-20% without inhibiting perchlorate reduction.

### **4.3.3 Evaluation of Inorganic Co-Contaminants**

Several inorganic co-contaminants originating from propellant washout operations (propellant and case constituents) and propellant hydrolysis operations were evaluated for their effect on perchlorate reduction performance.

**Boron** Only the highest concentration of boron tested (500 ppm) appeared to inhibit perchlorate biodegradation. However, boron can bio-accumulate and affect microbial growth. If significant boron is anticipated in process wastewater for a prolonged period of time, consideration should be given to wasting all the biomass generated in the process.

**Cadmium** Some inhibition or loss of performance occurred in the presence of high cadmium concentrations greater than 42 ppm although proper acclimation of the culture may result in acceptable perchlorate reduction as was evidenced by bottle tests at 208 and 833 ppm.

**Aluminum Hydroxide** Slight inhibition of perchlorate reduction may have occurred at higher aluminum concentrations (150 - 300 ppm).

## **4.4 IMPROVED OPERATIONAL PERFORMANCE**

During May 1999, the prototype process was transitioned from a brewer's yeast/cheese whey mixture to whey, then to a whey/CBP mixture, and finally to CBP in a period of five weeks. Additional micronutrients were fed to the process during this transition. The existing nutrient pumps performed well with the new nutrient, although some nutrient dilution was required to maintain the required flow rate.

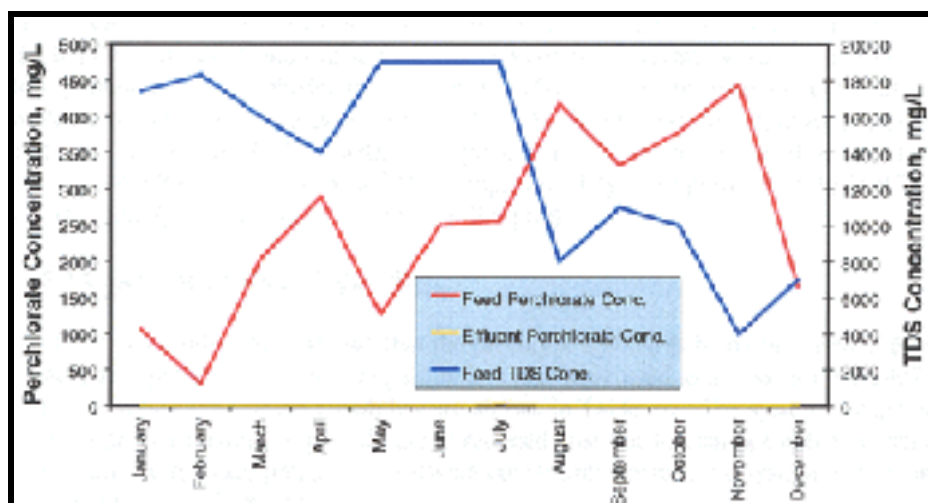
Steady state conditions were attained at residence times between 10-20 hours. The reactors performed extremely well in the single-stage (parallel) configuration despite being fed varying concentrations of perchlorate and TDS. It was necessary to dilute the brine feed to 5-20% of its original concentration to maintain reactor TDS at acceptable levels and to maintain perchlorate feed concentration near to the optimum 4,000 ppm. A summary of the Thiokol operational data for 1999 is shown in Table 3 below. The sodium perchlorate and TDS concentrations in the raw brine feed varied significantly. A total of 84,321 gallons of brine containing 7.7 tons of perchlorate from Thiokol's perchlorate recovery and ion exchange units were treated. Occasionally, other effluents and

inorganic contaminants were processed through the system. For example, 0.14% IPA waste stream was processed 10-17 February.

**Table 3. Summary of Effluent Treated at Thiokol in 1999.**

Month	Volume of Brine Treated (gallons)	Average $\text{ClO}_4^-$ Concentration (mg/l)	Perchlorate Destroyed (lbs.)
January	6,128	10,232	527
February	6,465	2,797	152
March	3,173	36,009	961
April	3,827	41,303	1,330
May	4,979	16,271	681
June	7,790	18,559	1,216
July	9,294	16,716	1,307
August	9,812	24,735	2,041
September	8,960	21,830	1,645
October	11,626	19,442	1,901
November	8,151	39,567	2,713
December	4,116	26,788	927
Total	84,321		15,402

Figure 6 shows the weighted-average monthly concentrations of perchlorate and TDS processed in the reactors (after dilution) and the resulting treated effluent concentrations. The TDS in the feed stream dropped following the switch to CBP nutrient. The monthly average perchlorate feed concentration delivered to the reactors varied from 305 mg/l to 4,624 mg/l. The TDS concentration fed to the reactors ranged from 4000 to 19,000 mg/l. Figure 7 shows the daily variation in perchlorate feed concentration for the month of June 1999 and the resulting effluent perchlorate concentration.



**Figure 6. Reactor Perchlorate and TDS Concentration (Thiokol 1999 Operation).**

Effluent perchlorate concentration was measured prior to discharge at the effluent storage tanks by the perchlorate ISE analyzer. The monthly average treated effluent concentrations ranged from 2.74 and 24.95 ppm using this method. Spot checks of samples using laboratory IC low concentration methods confirmed that samples reading 0-30 ppm using the ISE method were actually non-detect to low ppb (4-400 ppb).

The residual COD and TSS levels in the treated effluent were each as high as 5,000 ppm. The effluent was discharged directly to the sewer. The TSS consisted mostly of biomass that grew under steady state operation of the CSTR reactors. Direct sewer discharge might be allowable if the process were implemented elsewhere, otherwise further treatment would be necessary to treat the residual organic content.



**Figure 7. Variation of Perchlorate Concentration in Reactor Feed Composite (Thiokol June 1999 Operation).**



Biological processes are inherently stable, reliable, simple, cost-effective processes. The microbes used in this process, while enriched and specialized, are naturally occurring and very stable in the environment required to reduce perchlorate. As long as perchlorate-reducing conditions were maintained, the consortium of perchlorate-reducing microbes remained dominant. The HAP-1 organism was not lost or displaced after months of operation in unsterile environments, except when the reactor was exposed to excess oxygen, high temperature, or extreme pH.

#### 4.5 REVISED PROCESS CAPABILITY

During 1999, stable operation at a residence time as low as 12 days was achieved and performance objectives were met. The tolerance to the influent TDS level in the diluted brine was also increased due to acclimation of the reactor biomass population. The system was thought capable of processing an even greater amount of perchlorate following the switch to CBP nutrient supplementation. Laboratory studies indicated that the prototype system was being operated at only 25-40% of its potential capacity. Although biological processes are generally slow, high perchlorate reduction rates ( $> 0.5 \text{ g/l/hr}$ ) may be achievable at very short residence times (4-8 hours). However, equipment and software constraints inherent in the prototype design prevented the system from being operated at optimal performance. Performance parameters that were used as a basis for the 1997 configuration versus the current capability are shown in Table 4.

**Table 4. 1997 Design Basis vs. Current (1999) Capability.**

Reactor Performance Parameters (diluted brine)	1999 Design Bases for Prototype	1999 Design Bases for Full-Scale Plant
Retention Time, hours	18-36	4-8
Operating Temperature, °C	35-40	< 20
Perchlorate Treatment Range	1,000-15,000 ppm	1-15,000 ppm
Perchlorate Destruction	< 1 ppm	< 4 ppb
Brine Tolerance, TDS	< 2.2%	> 5%
Co-contaminants Reduced	$\text{NO}_3^-$	$\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{ClO}_3^-$ , Cr (VI)
Nutrients	Brewer's Yeast Yeast-Whey Blends	Carbohydrate Food Processing Byproducts

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## 5.0 COST ASSESSMENT

Costs associated with startup, including equipment, design engineering, site preparation, installation, and labor were prepared. Figure 5 shows the budgetary cost estimates for a full-scale treatment plant slightly larger than the Thiokol prototype. The process design was two 1600-gallon reactors operated in series, with a design capacity 2-4 times greater (~4 gpm diluted brine). The commercial system would be skid mounted like the Thiokol prototype but the controls would be simplified and the materials of construction mostly fiber reinforced plastic (FRP) and high-density cross-linked polyethylene (HDPE). Operational and maintenance (O&M) cost estimates in Table 5 were derived from actual costs for operating the Thiokol prototype.

Due to the uncertainty in extrapolating the performance of the prototype to a full-scale plant, life-cycle cost calculations were also made for two higher-performance scenarios in order to cover the possible range of performance anticipated for a full-scale implementation. The costs for the two additional scenarios are provided in Figures 6 and 7. (The equipment cost estimates in Figures 6 and 7 are slightly higher due to larger brine, dilution water and nutrient feed pumps.) The life-cycle treatment cost would vary depending on the concentration of the brine to be treated and on the reactor performance achievable on a full-scale implementation

**Case 1.** (Figure 5) Residence Time = 12 hr. (4 gpm feed rate of diluted brine)

Maximum productivity demonstrated by the prototype (with pump/control valve size limitations). Life-cycle treatment cost \$0.35 to \$1.40 per gallon undiluted brine.

**Case 2.** (Figure 6) Residence Time = 8 hr. (6 gpm feed rate of diluted brine)

Realistic reactor productivity expectation for a full-scale installation based on projections from recent laboratory work. Life-cycle treatment cost \$0.25 to \$1.00 per gallon undiluted brine.

**Case 3.** (Figure 7) Residence Time = 4 hr. (12 gpm feed rate of diluted brine)

Optimistic reactor productivity expectation for a full-scale installation based on probable minimum residence time before process instability due to biomass washout. Life-cycle treatment cost \$0.15 to \$0.60 per gallon undiluted brine.

The range for life-cycle treatment costs was \$0.15 to \$1.40 per gallon undiluted brine, including a surcharge of \$0.05 per gallon undiluted brine for direct discharge to sewer (or for residual effluent treatment). This indicates significant potential for savings compared to the \$1.00 per gallon cost of conventional processing. On a normalized basis, the average life-cycle treatment cost would range from \$1.30 to \$3.10 per lb perchlorate destroyed. The most optimistic reactor productivity (Case 3) would yield a payback of 2.5 - 6.5 years on the initial fixed costs, if conventional processing were replaced by the biodegradation system.

### Assumptions Used in Cost Calculations:

Simple amortization of fixed startup costs over a 10-yr lifetime for the process equipment. No salvage value for equipment was credited. Discounted cash flow analysis was not justified because of the wide possible performance range, which was captured by the unit costs yielded by the three case studies.

Labor requirement = 1 shift, 8 hr/d, 50% time (due to automatic process control)  
Labor cost = \$24/hr  
Electricity cost = \$0.075/kWh

Brine concentration = 10,000 - 80,000 ppm perchlorate  
(as received) = 0.085 - 0.70 lb perchlorate per gallon brine  
Brine dilution = 5% - 20 %  
Diluted brine feed = 2,000 - 4,000 ppm perchlorate  
= < 10,000 ppm TDS

Cost of CBP nutrient = \$25/ton (\$0.14/gallon) = \$0.01/lb  
CBP requirement = 10 gm/l = \$0.0008 per gallon diluted brine  
Add 25% for cost of additional micronutrients  
Total nutrient cost = \$0.001 per gallon diluted brine  
= \$0.005 - \$0.02 per gallon raw brine  
= \$ 0.06 - \$0.24 per lb perchlorate

Residual COD treatment cost = \$0.0015-0.006 per gallon (for 500-2,000 ppm COD)  
Residual TSS treatment cost = \$0.001-\$0.0035 per gallon (500-2,000 ppm TSS)  
Total COD + TSS cost = \$0.0025-\$0.01 per gallon (average \$0.006 per gallon)  
= \$0.05 per gallon undiluted brine  
= \$0.07-\$0.60 per lb perchlorate

**Table 5. Cost for Commercial 4 GPM Process (Case 1).**

<b>Cost Data (in \$1,000)</b>				
<b>Cost Category</b>	<b>Start-up</b>	<b>Annual O&amp;M</b>	<b>Demobilization</b>	<b>Life-Cycle</b>
Labor	20	35	-	-
Training & O&M Manual Prep.	35	-	-	-
Site-Specific Treatability Studies	100	-	-	-
Design/Engineering	80	-	-	-
Site Preparation	100	-	-	-
Equipment Installation	75	-	-	-
Analysis/Monitoring	15	5	-	-
Contracting	-	-	-	-
Permits/Regulatory Requirements	-	-	-	-
Capital Equipment	225	-	-	-
Modifications	-	-	-	20
Scheduled Maintenance	-	20	-	-
Consumables	-	-	-	-
Nutrients		2		
Acid, Caustic, Chemicals		1		
Electricity		14		
Ancillary Equipment	-	-	-	-
Effluent Treatment (for residual COD/TSS)	-	13	-	-
Equipment Decontamination	-	-	5	-
Equipment Removal	-	-	15	-
Site Restoration	-	-	-	-
Future Liability	-	-	-	-
Sub-Total (in \$1,000)	650	80	20	20
Sub-Total 10-yr Life-Cycle Costs (in \$1,000)	650	800	20	20
Total 10-yr Life-Cycle Costs (\$)	\$1,490,000			
Life-Cycle Cost (\$ per gallon brine)	\$0.35-\$1.40			
Residual COD/TSS Cost (\$ per gallon brine)	\$0.05			
Life-Cycle Cost (\$ per lb. perchlorate destroyed)	\$2.00-\$4.20			
Life-Cycle Cost (Av. \$ per lb. perchlorate destroyed)	\$3.10			

**Table 6. Cost for Commercial 6 GPM Process (Case 2).**

<b>Cost Data (in \$1,000)</b>				
<b>Cost Category</b>	<b>Start-up</b>	<b>Annual O&amp;M</b>	<b>Demobilization</b>	<b>Life-Cycle</b>
Labor	20	35	-	-
Training & O&M Manual Prep.	35	-	-	-
Site-Specific Treatability Studies	100	-	-	-
Design/Engineering	80	-	-	-
Site Preparation	100	-	-	-
Equipment Installation	75	-	-	-
Analysis/Monitoring	15	5	-	-
Contracting	-	-	-	-
Permits/Regulatory Requirements	-	-	-	-
Capital Equipment	235	-	-	-
Modifications	-	-	-	20
Scheduled Maintenance	-	20	-	-
Consumables	-	-	-	-
Nutrients		3		
Acid, Caustic, Chemicals		2		
Electricity		5		
Ancillary Equipment	-	-	-	-
Effluent Treatment (for residual COD/TSS)	-	19	-	-
Equipment Decontamination	-	-	5	-
Equipment Removal	-	-	15	-
Site Restoration	-	-	-	-
Future Liability	-	-	-	-
Sub-Total (in \$1,000)	660	89	20	20
Sub-Total 10-yr Life-Cycle Costs (in \$1,000)	660	890	20	20
Total 10-yr Life-Cycle Costs (\$)	\$1,590,000			
Life-Cycle Cost (\$ per gallon brine)	\$0.25-\$1.00			
Residual COD/TSS Cost (\$ per gallon brine)	\$0.05			
Life-Cycle Cost (\$ per lb. perchlorate destroyed)	\$1.40-\$3.00			
Life-Cycle Cost (Av. \$ per lb. perchlorate destroyed)	\$2.20			

**Table 7. Cost for Commercial 12 GPM Process (Case 3).**

<b>Cost Data (in \$1,000)</b>				
<b>Cost Category</b>	<b>Start-up</b>	<b>Annual O&amp;M</b>	<b>Demobilization</b>	<b>Life-Cycle</b>
Labor	20	35	-	-
Training & O&M Manual Prep.	35	-	-	-
Site-Specific Treatability Studies	100	-	-	-
Design/Engineering	80	-	-	-
Site Preparation	100	-	-	-
Equipment Installation	75	-	-	-
Analysis/Monitoring	15	5	-	-
Contracting	-	-	-	-
Permits/Regulatory Requirements	-	-	-	-
Capital Equipment	225	-	-	-
Modifications	-	-	-	20
Scheduled Maintenance	-	20	-	-
Consumables	-	-	-	-
Nutrients		6		
Acid, Caustic, Chemicals		3		
Electricity		8		
Ancillary Equipment	-	-	-	-
Effluent Treatment (for residual COD/TSS)	-	38	-	-
Equipment Decontamination	-	-	5	-
Equipment Removal	-	-	15	-
Site Restoration	-	-	-	-
Future Liability	-	-	-	-
Sub-Total (in \$1,000)	680	115	20	20
Sub-Total 10-yr Life-Cycle Costs (in \$1,000)	680	1,150	20	20
Total 10-yr Life-Cycle Costs (\$)	\$1,870,000			
Life-Cycle Cost (\$ per gallon brine)	\$0.15-\$0.60			
Residual COD/TSS Cost (\$ per gallon brine)	\$0.05			
Life-Cycle Cost (\$ per lb. perchlorate destroyed)	\$0.85-\$1.75			
Life-Cycle Cost (Av. \$ per lb. perchlorate destroyed)	\$1.30			

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## 6.0 IMPLEMENTATION ISSUES

Several modifications to the Thiokol prototype are recommended.

### 6.1 PERFORMANCE OBSERVATIONS

- The computer and control software packages are obsolete and should be upgraded. Physical modifications would also involve minor software changes.
- Bench scale studies have shown that the system operates more effectively in series at shorter residence times (4-8 hrs.). Installing larger control valves (increased Cv) and flowmeters would provide the system with the capability of operating at reduced residence times. Increased dilution water flow rate is necessary along with increased brine flow rate to maintain feed TDS and perchlorate concentration at acceptable levels.
- The process would operate efficiently at a temperature of 25°C or less to reduce heating cost. To operate at lower temperatures, the oversized glycol circulation pump would need to be replaced. The system could then be run at ambient temperatures (20-35°C) during warmer times of the year and be more easily controlled during colder times of year.
- Nutrient supplementation was provided as a separate feed to the reactor. It is important to maintain an independent nutrient feed for start-up and upset recovery. While using the brewer's yeast and cheese whey nutrient mixture, nutrient feed contamination was a problem in the nutrient storage tank. Some feed contamination continued to occur with diluted CBP. Feeding undiluted CBP would prevent nutrient contamination because concentrated CBP will not support bacterial growth. Feeding concentrated nutrients would also result in smaller vessels and lower cost, and using dosing pumps rather than a magnetically driven pump for nutrient feed would allow nutrient flow control valves to be removed from service.
- The clarifier and recycle pump should be removed from service. Although it may be possible to employ 100% solids recycle with very dilute feeds for which minimum nutrient addition would be required, the ability to waste a portion of the organic solids is absolutely necessary for higher perchlorate and nutrient concentrations. In this case, bench scale studies have shown that the solids or cell recycle is not necessary and at times harmful to the process. Recycled effluents and cells may result in bioaccumulation of co-contaminants, which can inhibit perchlorate reduction. Treated effluent from the reactors should instead be fed to a larger intermediate holding tank before discharge to the sewage treatment plant.

### 6.2 COST OBSERVATIONS

- Successful use of the alternate CBP nutrient supplementation reduced cost to such an extent that it was no longer a major cost driver. By switching from a brewer's yeast/cheese whey mixture to CBP for nutrient supplementation, nutrient costs were reduced from \$1.76 to \$0.16 per pound of perchlorate treated, or over a 90% cost reduction. Although nutrient requirements increase proportionally with feed rate, the unit cost per gallon of perchlorate feed remains constant, once the optimum dilution of the feed (to 4,000 ppm) has been established.

- The major cost driver is the capital cost of the process equipment. However, improving reactor productivity and plant capacity by operating the reactors in the preferred series mode, making recommended equipment modifications, and using lower-cost construction materials, would diminish the effect of the capital cost driver.
- A better choice of construction materials may result in a more reliable and less expensive implementation. Many of the original vessels fabricated from stainless steel (304) showed signs of significant corrosion in places. However, components and vessels fabricated out of fiberglass reinforced plastic (FRP) and high-density polyethylene (HDPE) performed very well. The cost analysis was based on FRP reactors.
- Labor is the other major cost driver. Labor is not a full-time requirement, and the cost could be reduced if labor resources could be spread over other AP recovery and treatment operations.
- The high residual COD and TSS levels in the treated effluent are a cost driver in the overall perchlorate treatment process because an additional treatment surcharge would likely be levied by the receiving sewage treatment facility before accepting direct discharge to the sewer.
- Caustic sterilization of the nutrient reduced chemical costs. Since acid-generating reactions occur in the reactor, the caustic nutrient feed could be manipulated in a way to nearly eliminate acid addition for pH control. Other nutrient sterilization techniques (steam), or direct feeding of dry nutrients, may further reduce operating costs.

### **6.3 SCALE-UP ISSUES**

The prototype operation at Thiokol represented an approximately 500-fold scale-up of the previous laboratory scale systems with no apparent problems. Biomass flocking was more efficient in the prototype system. This resulted in increased biosolids in the reactor, improved clarification, and improved performance overall. Large-scale installations are possible using the CSTR design. Reactors with 20-30,000 gallon capacities can be shop-fabricated. Larger capacity systems could be easily implemented by configuring multiple CSTRs. If necessary, packaged anaerobic and aerobic process would be available for residual COD reduction.

### **6.4 LESSONS LEARNED**

Lessons learned from previous start-ups were successfully employed for both the Tyndall AFB and Thiokol demonstrations. It was important to remove nearly all of the oxygen and minimize dilution of the inoculum in the reactor. This, coupled with excess nutrient and low initial perchlorate concentrations (500-1000 ppm), resulted in effective and rapid reactor inoculation.

The prototype demonstrated at Thiokol was much more complex in design than is necessary for typical wastewater treatment. The degree of control was also very high compared to a typical biological process. Future application of this process could be greatly simplified by employing local control with computer monitoring versus the PLC type system.

This prototype system was designed with two reactors, two effluent storage tanks, and a clarifier. This multiple vessel approach was very beneficial. More reactors provided a margin of safety in case of an upset. A reactor could be quickly re-inoculated from the other reactor or storage tanks. Moreover, small reactors versus one large reactor made start-up inoculation easier.

This process was specifically designed to permit the addition of two separate effluent streams to minimize the possible generation, through cross reactions, of compounds detrimental to the biological process. However, during conversion from parallel to series operations, potassium-containing brine remaining in inadequately flushed feed lines was able to mix with ammonium perchlorate, and the resulting potassium perchlorate precipitation caused plugging.

## **6.5 END-USER ISSUES**

This technology could be applied at other DoD and propulsion manufacturer facilities that generate similar waste streams. This process was developed to treat perchlorate in the presence of inorganic contaminants. In laboratory studies, perchlorate could also be reduced in the presence of organic and other energetic materials.

This technology is adaptable to fixed-film biological processes. Fixed-film processes such as the fluidized bed reactor (FBR) have the potential to efficiently treat effluents with low perchlorate concentrations (<100-500 ppm). They utilize nutrient more efficiently and may demonstrate shorter hydraulic residence times. However, for higher perchlorate concentrations, the CSTR system is very efficient and is the preferred approach.

Groundwater remediation may be accomplished using the same organism. Envirogen, Inc., Lawrenceville, NJ ([www.envirogen.com](http://www.envirogen.com)) has installed a full-scale, anaerobic FBR biodegradation process at the Gencorp Aerojet facility in Sacramento, California to treat successfully up to 4,000 gpm of groundwater containing up to 10 ppm perchlorate.

## **6.6 REGULATORY ISSUES**

Each demonstration facility complied with its State Implementation Plan and NPDES permit requirements. The shipping of “samples” for treatability studies to Tyndall AFB, required permission from the Florida Department of Environmental Protection coordinated through local and base officials. The demonstration at Thiokol required no new permits. Activities associated with modification of the existing IWTP were within the scope of existing permits.

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## APPENDIX A

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